THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

I. The Stereoisomers of Dichloro-Diethylenediamine Platinic Chloride

II. Studies on the Configurations of Ammines of Cadmium, Zinc, Platinum, and Cobalt

III. Stereochemistry of the Saturated Tervalent Nitrogen

BY

FRED BASOLO

B. Ed., Southern Illinois State Normal University, 1940
M.S., University of Illinois, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1943

URBANA, ILLINOIS
1943

THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

I. The Stereoisomers of Dichloro-Diethylenediamine Platinic Chloride

II. Studies on the Configurations of Ammines of Cadmium, Zinc, Platinum, and Cobalt

III. Stereochemistry of the Saturated Tervalent Nitrogen

BY

FRED BASOLO

B. Ed., Southern Illinois State Normal University, 1940
M.S., University of Illinois, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1943

URBANA, ILLINOIS
1943

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. J. C. Bailar, Jr., who suggested and directed these investigations, for his continued interest and guidance throughout the course of this work.

Special thanks are due Professor W. H. Rodebush for a theoretical interpretation of ultra-violet absorption spectra, Dr. H. A. Laitinen for polarographic studies, Mr. V. A. Yarborough for dielectric constant measurements, Mr. M. DenHerder for aid in the use of the ultra-violet apparatus, and Mr. J. A. Howsmon for x-ray diffraction patterns.

THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

I. The Stereoisomers of Dichloro-Diethylenediamine Platinic Chloride

Dichloro-diethylenediamine platinic chloride, $[Pt\ en_2Cl_2]Cl_2$ was first announced by Kurnakov[1]. He prepared it by passing an excess of chlorine through an aqueous solution of $[Pt_2\ en_2]Cl_2$. Only one form of this salt was isolated and several years later Schleicher, Henkel, and Spies[2] attempted to show that this compound has the *trans* configuration. Their work on the structure of $[Pt\ en_2Cl_2]Cl_2$ was soon questioned by Chernyaev and Rubinshtein.[3] It was, therefore, believed that the problem of isolating and proving the structure of the *cis* and *trans* forms of $[Pt\ en_2Cl_2]Cl_2$ should be undertaken.

Determinations of the configuration of stereoisomeric series depend largely on the fact that bifunctional groups can, from consideration of molecular dimensions, span only *cis* positions. Provided that no intramolecular change of configuration occurs during reaction, the isomer which is formed by displacement of such a group, must belong to the *cis* series. With this in mind Rapp[4] devised a successful preparation of what were assumed to be the two stereoisomeric forms of $[Pt\ en_2Cl_2]Cl_2$. A consideration of the structures of these two stereoisomers reveals the fact that the *trans* form is symmetrical whereas the *cis* form is not symmetrical and may exist in two optically active forms. Rapp attempted to prove the structures of the *cis* salt by separating it into its optically active antipodes but failed due to the fact that the salts obtained were too soluble to permit good fractional crystallization.

In an attempt to obtain a less soluble compound, the analagous dibromo complex was prepared. All attempts to resolve this yellow $[Pt\ en_2\ Br_2]Br_2$ failed. It seemed that perhaps

the difficulty in resolving this salt might be due to rearrangement of the *cis* form to the symmetrical *trans* form. It is known that a carbonato group cannot "reach" *trans* positions and, therefore, $[Pt\ en_2CO_3]CO_3$ is not capable of rearranging. Unsuccessful attempts were made to separate this compound into its two optical isomers.

It has been observed that in coordination compounds, negative groups activate the *trans* position.[5] On this basis it would seem that replacement reactions should proceed more readily with *trans* $[Pt\ en_2Cl_2]Cl_2$ than with the corresponding *cis* salt. This was shown to be true in so far as liquid ammonia at -33° displaced one of the coordinated chlorine groups in the supposed *trans* salt but failed to react with the *cis* form.

X-ray diffraction patterns of powdered samples revealed that the two forms were not the same. Assuming that the *trans* salt has a zero dipole moment, an approximate value of 1.49×10^{-18} e. s. u. was obtained for the dipole moment of the *cis* compound.

Ultra-violet absorption spectra reveal that a third band appears in all coordination compounds having at least one pair of negative groups in *trans* positions to each other.[6] It was found that *trans* $[Pt\ en_2Cl_2]Cl_2$ gave a third band at 2575A° whereas the *cis* form lacked such a band. It was suggested that perhaps the greater absorption of the *trans* salt could be due to the fact that the coordinated ethylenediamine molecules form coplanar rings,[7] rather than to the presence of negative groups in *trans* positions as was posulated by Tsuchida. In an attempt to test this suggestion, the ultraviolet absorption spectra of several selected coordination compounds were taken. These spectra strengthen the theory of Tsuchida.

II. STUDIES ON THE CONFIGURATIONS OF AMMINES OF CADMIUM, ZINC, PLATINUM, AND COBALT

Although the absolute configurations of a pair of optical

isomers are not known for any compound at the present time, the relative space positions of some compounds may be found if the configuration of a given compound be designated. The space relationships of the trioxalate coordination compounds of cobalt, chromium, rodium, and iridium has been found by three independent means: (1) "Cotton effect" or circular dichroism,[8] (2) Werner's solubility rule,[9], and (3) Delepine's "active racemate" method.[10] It was believed that this last work should be extended to include complex ions of different valences.

Some success was attained in relating the configurations of tri-diamines of platinum, cadmium, and zinc.[11] The result in the active racemate study fell short of what was expected because of the failure encountered in preparing crystals of $[Pt\ d\text{-}pn_3](CO_3)_2$. It was believed that perhaps the use of butylenediamine in place of propylenediamine might change the solubility of the platinum complex sufficiently to allow the formation of good crystals. This compound, $[Pt\ m\text{-}bn_3](CO_3)_2$, was prepared but was too soluble to yield large crystals.

Compounds in which amino alcohols behave as bidentate donor groups were prepared for the first time. These compounds were very unstable and it was only possible to isolate coordination compounds of zinc and cadmium.

Since all attempts to form crystalline hexacoordinated platinic carbonate using different coordinating groups failed, attempts were made to prepare other complex salts which might be isomorphous with similar salts of cadmium, zinc, and cobalt. Various anions of the correct valence were found in the literature, and the *racemic*-tripropylenediamine salts of these were studied. Crystals suitable for crystallographic studies could be obtained only in the cadmium and zinc series. In the platinum series the complex carbonate, sulfate, selenate, titanate, and stannate are too soluble, while the cobaltocyanide and ferrocyanide are insoluble. Similarly the complex cobaltic phosphate is too soluble, whereas the cobalticyanide and ferricyanide are insoluble.

III. STEREOCHEMISTRY OF THE SATURATED TERVALENT NITROGEN

One of the chief problems which has for a long time been discussed in connection with the constitution of complex metallic salts concerns the nature of the linkage between the coordinated molecules of the donor groups and the central atom. A consideration of the properties of such salts show that the linkage between the donor molecule and the metal atom must be covalent, since it persists in solution without ionization. Thus, if the linkage between a nitrogen donor and a metal is the same as the linkage between the nitrogen and oxygen in amine oxides, it seems logical that coordination of an asymmetric tertiary amine to a metal should give a resolvable asymmetric nitrogen. However, because tertiary amino groups usually coordinate very feebly, if at all, with metallic atoms the work done has necessarily been confined to secondary amino groups. Two conflicting reports [12, 13] appear in the literature and, therefore, it was thought that a coordination compound containing an asymmetric saturated tervalent nitrogen should be prepared.

Potassium dichloro-sarcosine platinite, $K[PtSrCl_2]$, and potassium trinitro-sarcosine-ammine cobaltiate, $K[CoNH_3Sr(NO_2)_3]$, were prepared. All attempts to resolve these two compounds which contain an asymmetric saturated tervalent nitrogen failed. This seemed to indicate that such a nitrogen is not resolvable. The work done by Meisenheimer[12] could not be duplicated.

BIBLIOGRAPHY

1. Kurnakov, Z. anorg. Chem. **17**, 226 (1896).
2. Schleicher, Henkel, and Spies, J. prakt. Chem. **105**, 31 (1922).
3. Chernyzev and Rubinshtein, Ann. inst. platine, No. **11**, 63 (1933); C. A. **28**, 3329 (1934).
4. Rapp, Thesis, Doctor of Philosophy, University of Illinois, 1941.
5. Chernyzev, Ann. inst. platine, **4**, 243 (1926); C. A. **21**, 2620 (1927).
6. Tsuchida and Koshimoto, Bull. Chem. Soc. Japan, **11**, 785 (1936).
7. Rodebush, W. H., Private Communication.
8. Jaeger, Rev. trav. chim. **38**, 171 (1919).
9. Werner, **Ber. 45**, 121, 865, 1228 (1912).
10. Delepine, Bull. soc. chim., [5], **1**, 1256 (1934).
11. Clapp, Thesis, Doctor of Philosophy, University of Illinois, 1941.
12. Meisenheimer, Angermann, Holsten, and Kinderlen, Ann. **438**, 269 (1924).
13. Mann, J. Chem. Soc. **1934**, 468.

VITA

The writer was born in Christopher, Illinois on February 11, 1920. He received his elementary education in the public schools of that city. He entered the Southern Illinois State Normal University, September, 1936, and received the degree of Bachelor of Education in June, 1940. He was enrolled in the Graduate School of the University of Illinois from the fall of 1940 to the fall of 1943. In February, 1942, the degree of Master of Science was conferred. He held a teaching assistantship in the University of Illinois from 1940 to 1942 and a University Fellowship during the academic year 1942-43.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0237